

Quarterly Progress Report on  
Standard Agreement No. 04-329  
For the Period  
December 1 2006 through April 30, 2007

***Development of an Improved VOC Analysis Method for Architectural Coatings***

Prepared for California Air Resources Board  
and the California Environmental Protection Agency

Dane R. Jones, Professor  
Max T. Wills, Professor Emeritus

Department of Chemistry and Biochemistry  
California Polytechnic State University

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### **Disclaimer-**

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## **Acknowledgements**

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## **I. Work This Reporting Period**

This report summarizes work performed on the project from December 1, 2006 through April 30, 2007.

### **A. Task 2 Activities**

During this time period, work was continued on Task 2 activities including

- Requesting, cataloging and splitting of samples
- Refinement of testing procedures
- Preliminary analysis of samples

We also continued our work with other groups involved in VOC analysis and methods. In particular, we participated in a VOC analysis study with the South Coast Air Quality Management District (SCAQMD). We also participated with two manufacturers of recycled paint products on projects to determine VOC levels in recycled paint.

### **B. Samples**

Samples of the 86 coatings chosen by CARB for analysis for this project were ordered directly from the manufacturer. To date we have received thirty-four samples. Several manufacturers have promised to send samples and we are following up to make sure samples are sent. A few manufacturers have declined to participate in the study. If samples cannot be secured directly from manufacturers within one month, they will be purchased from commercial vendors.

A list of the coatings indicating those samples we have requested is given in Table 1. These samples were typically supplied in one gallon containers, as requested. In one instance, only a five gallon sample was available. One manufacturer offered to supply samples of three different, but similar products although only one sample from this manufacturer was on the original sample list. Since we were unable to obtain some other samples of this type of coating from other manufacturers, we will substitute these additional samples. We are continually contacting those manufacturers who have not yet sent samples to determine if they are willing to send samples for analysis.

After thorough mixing, each sample was divided into four one quart samples to be used for testing by us and possibly by other laboratories as part of the validation study associated with this project. These samples are in lined one-quart metal paint cans. These samples are currently undergoing analysis. Initially, the density of each coating is determined using a weight per gallon cup. For two component coatings, the density of each component is determined separately. For single component coatings, the solids fraction is then determined using ASTM 2369. Great care is taken to insure consistent amounts of coating and water (or other suitable solvent) are used in the solids determination since we have determined in previous work that the amount of coating and water (or other solvent) can affect the results obtained, especially if high boiling materials are present. For two component coatings, the components are mixed in the appropriate ratio and a sample of the coating is analyzed using a procedure similar ASTM 2369 with no added solvent. Details are explained later in this report. Results of densities and fraction solids for coatings received are given in Table 2.

**Table 1. Coatings requested from manufacturers for analysis**

	Coating Category	WATERBORNE				SOLVENTBORNE			
		Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
1	Bituminous Roof	X							
2	Bituminous Roof		X						
3	Bituminous Roof	X							
4	Bituminous Roof	X							
5	Bond Breakers				X				
6	Bond Breakers				X				
7	Bond Breakers				X				
8	Concrete Curing Compounds				X				
9	Concrete Curing Compounds				X				
10	Concrete Curing Compounds				X				
11	Concrete Curing Compounds	X			X				
12	Driveway Sealer	X							
13	Driveway Sealer	X							
14	Driveway Sealer	X							
15	Driveway Sealer	X							
16	Dry Fog	X							
17	Dry Fog	X							
18	Dry Fog	X							
19	Faux Finishing		X						
20	Faux Finishing	X							
21	Faux Finishing		X		X				
22	Fire Resistive	X							
23	Fire Resistive					X			
24	Floor	X							
25	Floor							X	
26	Floor		X						
27	Form Release Compounds							X	
28	Form Release Compounds				X				
29	Form Release Compounds							X	
30	High Temperature								X
31	High Temperature								X
32	Industrial Maintenance					X			
33	Industrial Maintenance					X			
34	Industrial Maintenance					X			
35	Lacquers	X							
36	Lacquers						X		X
37	Lacquers								X
38	Lacquers						X		X
39	Low Solids	X			X				
40	Low Solids	X			X				
41	Magnesite Cement								X
42	Mastic Texture		X						
43	Mastic Texture	X							
44	Mastic Texture	X							
45	Metallic Pigmented	X							
46	Metallic Pigmented	X							
47	Metallic Pigmented		X						
48	Multi-Color	X			X				
49	Multi-Color	X							
50	Multi-Color	X							

**Table 1. Coatings requested from manufacturers for analysis (con't.)**

	Coating Category	WATERBORNE				SOLVENTBORNE			
		Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
51	Quick Dry Primer, Sealer, and Undercoater	X							
52	Recycled	X							
53	Roof	X							
54	Roof	X							
55	Roof	X							
56	Rust Preventative		X						
57	Sanding Sealers				X				
58	Shellacs - Clear						X		
59	Shellacs - Clear						X		
60	Specialty Primer, Sealer, and Undercoater	X							
61	Stains - Clear/Semitransparent				X				
62	Stains - Clear/Semitransparent				X				
63	Stains - Clear/Semitransparent								X
64	Stains - Opaque	X							
65	Stains - Opaque	X			X				
66	Swimming Pool					X			
67	Swimming Pool			X					
68	Swimming Pool					X			
69	Traffic Marking								X
70	Traffic Marking								X
71	Traffic Marking	X							
72	Varnishes - Clear		X	X					
73	Varnishes - Clear		X						
74	Varnishes - Clear			X					
75	Varnishes - Clear		X						
76	Varnishes - Semitransparent		X						
77	Varnishes - Semitransparent				X				
78	Waterproofing Concrete/Masonry Sealers	X							
79	Waterproofing Concrete/Masonry Sealers	X							
80	Waterproofing Concrete/Masonry Sealers	X			X				
81	Waterproofing Sealers	X							
82	Waterproofing Sealers				X				
83	Waterproofing Sealers	X			X				
84	Wood Preservatives	X			X				
85	Wood Preservatives				X				
86	Wood Preservatives	X			X				

**Table 2 Fraction solids and densities of coatings samples**

Two component coatings have densities for both a and b components; fraction solids is for mixed coating

Sample	fraction solids	density (lbs/gal)	density (g/L)
1	0.478	8.743	1047
3a	0.880	11.725	1405
3b		12.720	1524
4	0.526	8.637	1035
5	0.465	7.029	842
6	0.562	11.451	1372
7	0.363	9.145	1096
24	0.567	9.435	1130
25a	0.815	15.004	1798
25b		7.416	888
26a	0.565	8.563	1026
26b		14.933	1789
34	0.516	10.410	1247
35	0.543	11.207	1343
38	0.578	10.927	1309
39	0.474	8.440	1011
40	0.574	11.418	1368
41	0.499	10.317	1236
43	0.475	10.329	1237
45a	0.282	8.321	997
45b		6.766	811
50	0.643	11.634	1394
51	0.219	8.430	1010
55	0.433	10.328	1237
56	0.064	8.231	986
57-1	0.255	7.549	904
57-2	0.218	7.380	884
57-3	0.252	7.493	898
63	0.412	9.471	1135
64	0.200	8.584	1028
65	0.098	8.426	1009
75	0.532	7.319	877
83	0.505	10.534	1262
84	0.228	7.283	872
85	0.224	7.308	875
86	0.039	8.373	1003
87	0.245	6.954	833

### **C. Refinement of Testing Procedures**

During this reporting period we have concentrated on development of an analysis method for two-component coatings. These coatings present particular challenges for VOC determination. In principal, the method should duplicate, as closely as possible, the actual procedure use in the field to mix and apply the coating. Current methods, including EPA Method 24, often employ techniques very different from those used in the field. In particular, components may be mixed with a solvent during the fraction solids determination (ASTM 2369). Addition of a solvent may affect the rate of the cure reaction and result in incomplete cure. Also, insufficient time may be allowed for the coating to cure before testing for volatiles. We have attempted to eliminate these discrepancies and develop a method providing representative VOC levels for the coatings under actual use conditions. In this new method the multi-component mixture is allowed to cure in a sealed headspace vial in which the VOC emissions are retained. Addition of acetone containing an internal standard transfers the emissions into the solvent and gives a solution which can be analyzed by direct injection into a gas chromatograph. Since the method provides a direct determination of the individual VOCs it is also suitable for quantitative determination of amounts of any hazardous air pollutants (HAPs) in these coatings. The detailed procedure we developed for analysis of two-component coatings is given below.

We have also investigated modifications in ASTM 6886 for analysis of single component coatings other than low VOC water based architectural coatings. In particular, we have tested the use of isopropanol (2-propanol) as the solvent for this test, as a replacement for tetrahydrofuran (THF). Isopropanol is less hazardous than THF and provides an alternative solvent in the event one of the VOC components in a coating co-elutes with the THF in the gas chromatograph. Other THF replacement solvents being tested include acetone and methyl ethyl ketone (MEK).

#### **Analysis of One-component Coatings**

In our last report, we presented results using a modification of ASTM 6886 using water in place of THF as the solvent and ethylene glycol diethyl ether (EGDE) instead of p-cymene as the internal standard. During this reporting period we have begun analysis of other coatings and have investigated the use of isopropanol (2-propanol, IPA) as the solvent. IPA is less hazardous than THF. We also determined that 2-butanol, which is present in at least one of the coatings analyzed to date, co-elutes with THF under conditions of the method. The 2-butanol can be detected by changing the temperature program on the GC but a more satisfactory solution is to use another solvent not found in these coatings, in particular, IPA. IPA elutes much earlier from the GC column than EGDE or 2-butanol and does not co-elute with other VOCs.



## **Analysis of Two-component Coatings**

### **1. Summary of Test Method**

1.1 The components are mixed, a sample of the mixture is weighed into a 20mL headspace vial, the vial is sealed with a crimp cap, and the mixture is allowed to cure for 24 to 36 hours at room temperature. After the initial room temperature cure the sample is heated for 30 minutes at 110°C. After cooling, a known quantity of acetone containing an internal standard is added to the sealed vial and the contents are mixed. The solution containing the VOCs is then analyzed by gas chromatography.

### **2. Procedure**

2.1 Determine the density of the individual components of the multi-component coating using ASTM Method D1475. Convert the manufacturer's recommended volume mix ratio to a weight mix ratio. Using a suitable container, prepare approximately 100g of the mixture and mix using a spatula or paint shaker. Immediately after mixing, transfer approximately 100 mg of the mixture to a 20 mL headspace vial containing a paper clip and weigh to 0.1mg. Seal the vial with a crimp cap immediately after adding the coating mixture to the vial. Using an external magnetic stir bar, spread the coating mixture evenly over the bottom surface of the vial. Prepare two more samples in the same way. At the same time that the headspace vials are being prepared, transfer approximately 0.5 g of the mixture to each of three aluminum foil dishes (58 mm in diameter by 18 mm high) containing a paper clip stirrer and weigh to 0.1 mg. **DO NOT ADD ANY SOLVENTS TO THE ALUMINUM FOIL DISHES.** Using the paper clip stirrer, spread the coating mixture as evenly as possible over the bottom surface of the aluminum foil pans. Let the vials and aluminum foil dishes containing the coating mixture stand at room temperature for a 24 to 36 hour cure. After the room temperature cure, place the sealed vials and aluminum foil pans in an oven at 110°C. The vials should remain in the oven for 30 minutes and the aluminum foil pans should remain in the oven for 60 minutes. Determine the total volatile content of the coating mixture by reweighing the cooled aluminum foil pans and determine the weight loss. The weight loss represents the total volatile content of the multi-component coating.

2.2 Prepare a solution of ethylene glycol diethyl ether (EGDE) in acetone at a concentration between 1 and 1.5 mg EGDE per gram of solution. To prepare this solution, weigh 100 to 150 mg EGDE to 0.1 mg into a suitable container add approximately 100 g of HPLC grade acetone, weighed to the nearest 0.001 g, and mix the contents. The solution should be stored in a tightly stoppered container to prevent evaporation of acetone. Calculate the concentration of EGDE to the nearest 0.001 mg per gram of solution.

2.3 Using a dedicated glass syringe, add approximately 3 mL of the EGDE/acetone solution to each of the cooled, crimp-cap stoppered headspace vials containing the cured multi-component coating and determine the weight of solution added to each vial to the nearest 0.001 gram. Calculate the absolute amount of EGDE added to each vial. Mix the contents of each vial by shaking for 1 to 2 minutes. Remove the crimp cap and decant the solution into an appropriate clean vial and stopper with a Teflon-lined cap. This solution contains the VOCs (and HAPs) released from a known quantity of the multi-component coating and a known quantity of the internal standard EGDE.

2.4 Chromatograph the solution obtained in 2.3 using the same chromatographic conditions described in ASTM Method D6886. Identify and calculate the amounts of the individual VOCs relative to the internal standard. Sum the individual VOCs to obtain the total VOC fraction.

### 3. Results

#### 3.1 Sample ARB # 3 (Solvent based 2-component epoxy)

High Solids Epoxy (Fast Dry)

Mixing ratio by volume: 1 part resin to 1 part cure

Mixing ratio by weight: 1405 parts resin to 1524 parts cure

**Table 3 VOC by Direct GC Compared with Method 24, Sample ARB # 3**

	Run 1	Run 2	Average	Reported by manufacturer
Compound	fraction	fraction		
Furfuryl alcohol	0.0203	0.0200	0.0201	None
Ethylbenzene	0.0113	0.0109	0.0111	0.0149
Total Xylene	0.0679	0.0652	0.0665	0.0627
Aromatic -100	0.0280	0.0273	0.0276	
Total VOC fraction	0.1274	0.1233	0.1254	
Total volatile fraction by ASTM D2369	0.1197			
Density (Calcd)	1465			
Coating VOC by GC	184			
Coating VOC by Method 24	175			180

### 3.2 Sample ARB # 25 (Solvent based 2-component epoxy)

Epoxy Topcoat

Mixing ratio by volume: 3 parts A to 1 part B

Mixing ratio by weight: 2697 parts A to 444 parts B

**Table 4 VOC by Direct GC Compared with Method 24, Sample ARB # 25**

	Run 1	Run 2	Run 3		
Compound	fraction	fraction	fraction	Average	Reported by manufacturer
MEK	0.0366	0.0353	0.0350	0.0356	0.0460
1-Butanol	0.0801	0.0786	0.0750	0.0779	0.0800
PM Acetate	0.0241	0.0238	0.0222	0.0233	0.0240
Ethylbenzene	0.0084	0.0083	0.0079	0.0082	0.0010
Total Xylene	0.0450	0.0441	0.0422	0.0438	0.0530
Benzyl alcohol	0.0148	0.0142	0.0133	0.0141	0.0150
Total VOC fraction	0.2090	0.2041	0.1955	0.2029	0.2190
Total volatile fraction by ASTM D2369	0.1853				
Density (Calcd)	1571				
Coating VOC by GC	319				
Coating VOC by Method 24	291				325

### 3.3 Sample ARB # 26 (Waterborne two-component epoxy topcoat)

Waterborne Epoxy Topcoat

Mixing ratio by volume: 3 parts A to 1 part B

Mixing ratio by weight: 3078 parts A to 1789 parts B

**Table 5 VOC by Direct GC Compared with Data Reported by Manufacturer, Sample ARB # 26**

	Run 1	Run 2	Run 3		
Compound	fraction	fraction	fraction	Average	GC data reported by manufacturer
1-Propoxyethanol	0.0829	0.0804	0.0809	0.0814	0.0852
Aromatic -100	0.0130	0.0116	0.0132	0.0126	0.0133
Total VOC fraction	0.0959	0.0920	0.0941	0.0940	0.0985
Total volatile fraction by ASTM D2369	0.4354				
Density (Calcd)	1217				
Water fraction (Calcd)	0.3414				0.3588
Material VOC by GC	114				120
Coating VOC by GC	196				213

### 3.4 Sample ARB # 45

Waterborne Two-component Epoxy

Mixing ratio by volume: 2.37 parts A to 1 part B

Mixing ratio by weight: 69.5 parts A to 30.5 parts B

**Table 6 VOC by Direct GC Compared with Direct GC Data Provided by Manufacturer and a 3d Party Testing Laboratory, Sample ARB # 45**

	Run 1	Run 2	Run 3			
Compound	fraction	fraction	fraction	Average	GC data reported by manufacturer	Reported by 3rd Party Testing Lab using Method 24
UK	0.0016	0.0016	0.0015	0.0016		
1-Methoxy-2-propanol	0.0718	0.0721	0.0655	0.0698	0.0747	
UK	0.0011	0.0010	0.0009	0.0010		
UK	0.0005	0.0005	0.0005	0.0005		
UK	0.0007	0.0005	0.0005	0.0005		
UK	0.0012	0.0012	0.0018	0.0014		
UK	0.0006	0.0007	0.0006	0.0006		
Benzyl alcohol	0.0037	0.0038	0.0036	0.0037	0.0038	
Total VOC fraction	0.0812	0.0814	0.0747	0.0791	0.0785	
Total VOC fraction by Method 24						0.06500
Total volatile fraction by ASTM D2369	0.7176					0.7270
Density					1042	1047
Water fraction (Calcd)	0.6384				0.6377	
Water fraction (ASTM D3960)						0.6620
Material VOC by GC	82				82	68
Coating VOC by GC	246				244	223

### 3.5 Sample SCAQMD #1M

Water Based Two-component Urethane (Note: this coating was not on the original sample list)

Mixing ratio by volume: 3 parts A to 1 part B, reduced with 10% water

Mixing ratio by weight: 164.2 parts A to 47.1 parts B, reduce with 16.0 parts water

**Table 7 VOC by Direct GC Compared with Product Information Sheet and MSDS Data Provided by Manufacturer, Sample SCAQMD Industrial Maintenance 2K, #1M**

	Run 1	Run 2		
Compound	fraction	fraction	Average	Reported by manufacturer
UK	0.0002	0.0002	0.0002	
UK	0.0003	0.0003	0.0003	
UK	0.0007	0.0006	0.0007	
Butyl acetate	0.0244	0.0244	0.0244	0.0249
UK	0.0004	0.0004	0.0004	
UK	0.0005	0.0005	0.0005	
UK	0.0011	0.0011	0.0011	
Dipropylene glycol mono methyl ether	0.0037	0.0034	0.0035	
UK	0.0010	0.0009	0.0010	
UK	0.0006	0.0006	0.0006	
UK	0.0006	0.0006	0.0006	
UK	0.0004	0.0004	0.0004	
UK	0.0014	0.0014	0.0014	
UK	0.0005	0.0005	0.0005	
Total VOC fraction	0.0357	0.0353	0.0355	
Total volatile fraction by ASTM D2369	0.3776			
Density (calcd)	1275			
Water fraction (Calcd)	0.3421			
Material VOC by GC	45			40
Coating VOC by GC	80			<100

Calculation worksheet for IM Coating #1M

	mix formula, grams	density	Liters	grams of VOC	reported material VOC	reported coating VOC	Reptd butyl acetate, % by wt	Calcd % butyl acetate in mix
Part A	1642	1368	1.2003	13.2032	11	23		
Part B	471	1114	0.4228	58.7693	139	139	12	0.0249
water	160	1000	0.1600	0.0000	0	0		
Total	2273		1.7831	71.9725				
Density of mixture (calcd)		1275						
VOC of mixture (calcd from MSDS data)					40			
VOC of mixture (reported by manufacturer)						<100		



### 3.6 Sample SCAQMD #2M

Water Reducible Two-component Polyurethane (Note: this coating was not on the original sample list)

Mixing ratio by volume: Not given. Calculated as 1.99 parts A and 0.54 parts B and reduced with 10% water.

Mixing ratio by weight: 210.6 parts A to 62.4 parts B, reduce with 20 parts water

**Table 8 VOC by Direct GC Compared with Product Information Sheet and MSDS Data Provided by Manufacturer, Sample SCAQMD Industrial Maintenance 2K, #2M**

	Run 1	Run 2		Reported by manufacturer
Compound	fraction	fraction	Average	
UK	0.0002	0.0003	0.0003	
UK	0.0004	0.0005	0.0004	
UK	0.0004	0.0003	0.0004	
UK	0.0002	0.0002	0.0002	
Dipropylene glycol mono methyl ether	0.0017	0.0018	0.0017	
UK	0.0005	0.0006	0.0005	
Trimethylolpropane	0.0050	0.0051	0.0050	
Cyclohexane dimethanol	0.0006	0.0007	0.0007	
UK	0.0002	0.0003	0.0002	
Butylated hydroxytoluene	0.0003	0.0003	0.0003	
Total VOC fraction	0.0094	0.0101	0.0098	
Total volatile fraction by ASTM D2369	0.4154			
Density (calcd)	1075			
Water fraction (Calcd)	0.4056			
Material VOC by GC	11			
Coating VOC by GC	19			<30

Calculation worksheet for IM Coating #2M

	mix formula, grams	density	Liters
Part A	2106	1059	1.9887
Part B	624	1160	0.5379
water	200	1000	0.2000
Total	2930		2.7266
Density of mixture (calcd)		1075	
VOC of mixture (calcd from MSDS data)			
VOC of mixture (reported by manufacturer)	<30		

## **II. Future work**

We will continue work on Task 2 during the next reporting period. We will continue our efforts to secure the remaining samples and will expand our analyses to all types of coatings included in the sample inventory. We will also begin shipping samples to laboratories who have agreed to shadow our work on this project.

## **III. Overall progress of project.**

Project is on time and on budget.